DEHYDROCOUPLING OF METHANE BY SUPPORTED ORGANOMETALLIC COMPLEXES

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INTRODUCTION

Two possibilities exist for dehydrocoupling of methane to higher hydrocarbons: The first is oxidative coupling to ethane/ethylene and water that is the subject of intense current research interest. As Labinger[1] and others have recently pointed out, oxidative coupling has an apparent upper limit on yield of C_2 hydrocarbons of around 30% at atmospheric pressure. Non-oxidative coupling to higher hydrocarbons and hydrogen is endothermic, but in the absence of coke formation the thermodynamic yield of hydrocarbons varies between 25% at 827 °C and 65% at 1100 °C and atmospheric pressure.[2] Additionally, after separation the unreacted methane can be recycled unlike oxidative coupling. These numbers are very attractive and a number of recent reports have appeared that prove this concept.[3-9] Yamaguchi's results are particularly interesting because he reported $\approx 50\%$ conversion of methane and $\approx 85\%$ selectivity to "aromatic oil" at 1300 °C. These values are very close to the thermodynamic equilibrium values.
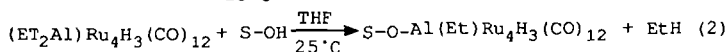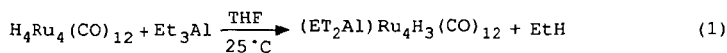
RESULTS AND DISCUSSION

Research on the technique of surface confinement to produce novel catalysts for a wide variety of processes is continuing in many laboratories.[10-13] We have been working on the development of novel surface confined catalysts to dehydrocouple methane. The catalysts are prepared by reacting organometallic complexes of transition metals with inorganic oxide supports to produce surface-confined metal complexes.[14] The increased activity of highly dispersed catalysts is desirable for activating the relatively inert methane and additionally highly dispersed catalysts are resistant to coking. The use of zeolitic supports will provide further stabilization of the highly dispersed catalysts which are confined inside the zeolite pores. The variables we are studying include cluster size, supporting materials, and reaction conditions.

Synthesis of catalysts- The synthesis of these catalysts involves three steps. The first step is to synthesize the ruthenium cluster precursors. The second step is a novel approach developed in our laboratory involving the reaction of the organometallic clusters with alkyl aluminum. The final step is to anchor these catalysts on supports by a chemical reaction between the hydroxy group of the support and the alkyl groups of the organometallic cluster to give a covalent chemical bond.

The organometallic complexes include: a mono-ruthenium complex, $Ru(allyl)_2(CO)_2$; a tetrameric ruthenium cluster, $H_4Ru_4(CO)_{12}$; a hexameric ruthenium cluster, $H_2Ru_6(CO)_{18}$; and a mixed metal cluster, $H_2FeRu_3(CO)_{13}$. All of these complexes are prepared according to literature procedures.[15,16] The hydrido clusters reacted with triethyl aluminum at room temperature (eq. 1). The reaction stoichiometries

are determined by measuring the quantity of ethane produced.[14] These alkyl aluminum carbonyl ruthenium clusters react with acidic supports: ß-alumina, 5A molecular sieves, and LZ-Y 52 zeolite. The reaction stoichiometries are again determined by measuring the quantity of ethane produced (eq. 2).

$$H_4Ru_4(CO)_{12} + Et_3Al \xrightarrow[25^\circ C]{THF} (ET_2Al)Ru_4H_3(CO)_{12} + EtH \qquad (1)$$

$$(ET_2Al)Ru_4H_3(CO)_{12} + S-OH \xrightarrow[25^\circ C]{THF} S-O-Al(Et)Ru_4H_3(CO)_{12} + EtH \quad (2)$$

The monomeric ruthenium complex reacts directly with the acidic support to release one equivalent of propylene. The tetraruthenium and the mixed iron-ruthenium clusters have also been supported on magnesium oxide by the reaction of the acidic hydride and the basic groups on the MgO surface. All supporting materials are in powder form except for the 5A molecular sieves which was 60-80 mesh.

The ruthenium catalysts were tested at 750°C under 150 psig pressure. The results are summarized in Table 1. We used a commercial ruthenium catalyst which is supported on alumina (obtained from Engelhard) for comparison. The metal loadings were based on elemental analyses (Galbraith Laboratory). The flow-rate of input gases (20% methane in helium) were varied due to the detection limit of our GC. Effect of flow-rate will be discussed later.

Effects of cluster size - The commercial ruthenium catalyst gives a very high conversion of methane (71.2%) but no hydrocarbon product. Methane conversion on the mono-ruthenium catalysts are considerably lower than the ruthenium clusters (Ru_4 and Ru_6). In general, methane conversions depend on the type of support and decrease in the order alumina, 5A molecular sieve, and zeolite. These results suggested that the methane conversion is related to the amount of surface bonded metal. On alumina, the metals are located on the surface while on 5A molecular sieves and on zeolite, increasing amounts of metal are located inside the zeolite pore. The Ru_4 catalysts demonstrated the greatest dependance on the support, the conversion decreased from 10.1 to 4.9 and to 1.7% on alumina, 5A molecular sieve, and Y-zeolite, respectively.

Our intention in using different supports is to confine the ruthenium cluster at different location on or within the support. Hence, the Ru_4 and Ru_6 clusters are dispersed on the alumina surface but are confined inside the pores of the zeolite supports. The pore size of the 5A molecular sieve is too small for the Ru_6 cluster but should be large enough for the Ru_4 cluster. Since the Y-zeolite has the largest pore (~17Å), most of the Ru_4 or Ru_6 clusters are located inside the zeolite pore.

Product selectivity - All the ruthenium catalysts produced C_2 hydrocarbons which included ethane and ethylene. The selectivity of C_2 hydrocarbon observed with Ru_4 cluster catalysts increased as the percent conversion of methane decreased. These results also suggest the advantage of having the metal cluster confined inside the zeolite cage. The Ru_6AL has the highest total hydrocarbon yield which is probably due to the higher metal loading. The total hydrocarbon yield for Ru_6MS and Ru_6ZL are about the same, but the Ru_6ZL has a higher selectivity for C_2 product. Confining the metal cluster inside the zeolite cage may also limited the propagation of methane polymerization. The ruthenium

monomers gave relatively low hydrocarbon yields indicating that polymerization of methane required more than one metal atom.

Coking - The results listed in Table 1 show that more than one equivalent of hydrogen was produced per methane reacted, which suggests coke formation. The elemental analyses listed in Table 2 show that the Ru4AL, Ru4MS, Ru6AL and Ru6MS catalysts contained more carbon after reaction with methane. In contrast, the carbon content of Ru4ZL decreased after reaction. This phenomena indicates that those catalysts that have metal dispersed on the support surface promote coke formation while the metals confined inside the zeolite cages do not. For Ru4MS, the carbon content only increased slightly to 4.38% as compared with more than 20% for the Ru4ZL which suggests that a portion of the metal clusters are located inside the cages of the support. The decrease of carbon content on Ru4ZL was due to the decomposition of the ruthenium complexes, i.e. release of carbon monoxide.

Effect of reaction conditions - The effect of reaction temperature is similar for every catalyst. Higher methane conversion and product yield are obtained at higher temperatures. Increasing the reaction pressure has a similar effect on the methane conversion. However, the product selectivities for hydrogen and C_2 hydrocarbons decrease but increases for C_{6+} hydrocarbons (Table 3). Highest selectivity is observed at 150 psig. As expected, increasing the space velocity lowers the methane conversion but increases the selectivity for hydrocarbon products.

Basic support and mixed metal cluster - Methane conversion over the magnesia supported ruthenium monomer and the FeRu3 cluster are much higher than the zeolite supported analogs (Table 4). However, the product selectivities to hydrocarbons are lower.

For the mixed iron-ruthenium catalysts, magnesia support also increases the methane conversion. At 600˚C, the methane conversion was 8.87% for FeRu3MgO and was 3.07% for FeRu3ZL. At 750˚C, methane conversion increased to 41.5% and 23.05% for FeRu3MgO and FeRu3ZL, respectively. These catalysts behave similarly to the ruthenium monomers that the hydrocarbon yields were lower on the magnesia supported catalyst.

In-Situ FTIR - In-Situ diffuse reflectance FTIR is being used to study these catalysts. Our diffuse reflectance FTIR (DRIFTS) technique is very similar to the ones recently reported by Vannice[17] and Moser.[18] We have been able to collect data using this system up to 600 °C.

Figure 1 demonstrates the kind of data that can be collected using this FTIR technique. In Figure 1 we have compared the thermal behavior of two of the clusters (FeRu3 and Ru4) supported on MgO under N_2. The carbonyl stretching region of the spectra is shown starting in the upper left at 25 °C. The two spectra are different as would be expected for the different clusters. The Ru4 spectra is very similar to that observed by Gates[19] for $H_4Ru_4(CO)_{12}$ adsorbed on magnesia and treated at 100 °C under He and very similar to the spectra observed by Guglielminotti for $Ru_3(CO)_{12}$ on magnesia.[20] The spectra of FeRu3 is similar to that observed by Basset and Shore on reacting $H_2FeRu(CO)_{12}$ with hydrated magnesia.[21] However, more dramatic is the difference in thermal behavior. The FeRu3 cluster has drastically changed by 200 °C and has completely disappeared by 300 °C. The Ru4 cluster is considerably more robust maintaining most of its features to 300 °C.

We then started with fresh samples and studied their IR behavior in flowing 5% methane in argon to simulate the conditions that we use in our dehydrocoupling experiments. The results were quite dramatic and are shown in Figure 2. The spectra are shown starting at 25 °C on the bottom left. Here clearly the $FeRu_3$ cluster begins to interact with the methane even at room temperature, while the Ru_4 has the identical spectra to that observed under nitrogen. Notice the increased intensity of the absorption, here over 6 units while under nitrogen the spectra of $FeRu_3$ had an intensity of less than 0.2 units, and also the loss of features (compare to upper left spectra of Figure 1). This broad absorption band is similar to a feature observed by Guczi[22] that was attributed to mobile subcarbonyls which arise from decomposition of the cluster. However, by 400 °C the two spectra have become identical (bottom right of Figure 2), a broad featureless absorption. This contrast to the spectra under nitrogen where by 400 °C both clusters and completely lost their absorption. We interpret these results as segregation of the metals. We hope next to study the C-H stretching region of the spectra to learn more about hydrocarbon fragments on the catalysts.

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Table 1

ACTIVITY OF RUTHENIUM CATALYSTS FOR METHANE DEHYDROGENATION[a]

Catalyst[b]	Ru(wt%)	Flow rate (mL/min)	Methane Conver(%)	% Selectivity[c] to H_2	C_2	$C_6^{\pm}$
Ru-com	0.50	50	71.2	151.0	--[d]	--
RuAL	0.35	10	3.0	139.9	2.8	--
RuMS	0.31	10	2.3	147.5	1.2	--
RuZL	0.37	10	1.7	177.5	2.6	--
Ru_4AL	0.61	100	10.1	78.6	1.62	--
Ru_4MS	0.49	100	4.9	146.6	3.52	--
Ru_4ZL	0.61	50	1.7	25.3	6.9	28.9
Ru_6AL	1.26	50	6.1	113.4	6.9	41.4
Ru_6MS	0.19	50	5.6	192.8	1.0	14.8
Ru_6ZL	0.20	50	3.6	161.9	3.6	10.0

[a] Reaction condition: temperature=750°C, pressure=150 psig
[b] Abbreviation: Ru-com=commercial ruthenium catalyst from Engelhard; $Ru_4=(C_2H_5)_2AlRu_4H_3(CO)_{12}$; $Ru_6=(C_2H_5)_2AlRu_6H(CO)_{18}$; $Ru=Ru(Allyl)(CO)_2$; AL=ß-alumina; MS=5A molecular sieve; ZL=LZ-Y zeolite.
[c] Selectivities were calculated on converted methane. Selectivity to hydrocarbons are based on carbon number.

[d] Not detected.

Table 2
ELEMENTAL ANALYSES OF RUTHENIUM CATALYSIS FOR METHANE REFORMING[a]

Catalyst	Before reaction			After reaction		
	%C	%H	%Ru	%C	%H	%Ru
Ru_4AL	5.09	1.04	0.61	26.50	0.40	0.57
Ru_4MS	1.46	1.13	0.49	4.38	0.46	0.64
Ru_4ZL	5.25	1.53	0.61	0.58	0.22	1.26
Ru_6AL	9.77	1.84	1.26	23.24	0.67	0.55
Ru_6MS	0.95	1.68	0.19	22.29	0.19	0.32

[a]Reaction with methane at 750°C for 15 h.

Table 3
EFFECT OF REACTION PRESURE AND SPACE VELOCITY TO THE ACTIVITY OF Ru_6ZL[a] AT 750°C

Pressure (psig)	Flow rate mL/min	%CH4 conversion	%Selectivity[b] of		
			H_2	C_2	C_{6+}
50	50	3.18	164.16	6.04	6.6
150	50	5.19	91.33	4.48	10.70
250	50	8.64	82.41	2.46	7.38
250	100	2.62	177.10	9.24	20.64

[a]Ru_6ZL = zeolite supported Ru_6 cluster, $C_2H_5AlRu_6H(CO)_{18}$.
[b]Selectivity was based on carbon number of hydrocarbon and the amount of methane reacted.

Table 4
CATALYTIC REACTIVITY OF ZEOLITE AND MAGNESIA SUPPORTED CATALYSTS FOR METHANE DEHYDROGENATION[a]

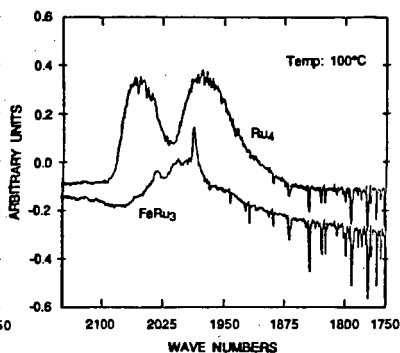| Catalysts	Temp(°C)	Methane Conversion(%)	Selectivity[b]	
			C_2(%)	C_{6+}
RuMgO	600	21.044	0.1	0.5
Ru_4MgO	750	4.04	6.9	49.2
$FeRu_3ZL$	600	3.07	1.9	18.5
$FeRu_3MgO$	600	8.87	0.1	--

[a]Reaction conditions: pressure=150psig, flow rate=20 mL/min, weight of catalyst=2 g, reactor O.D.=3/8in (S.S.).
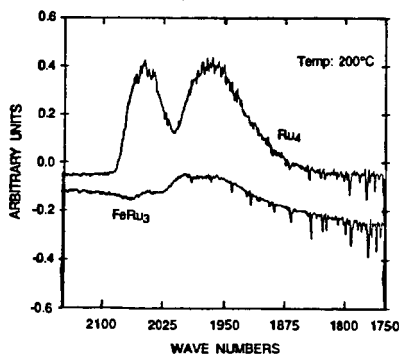[b]Selectivity to hydrocarbon is based on carbon number.
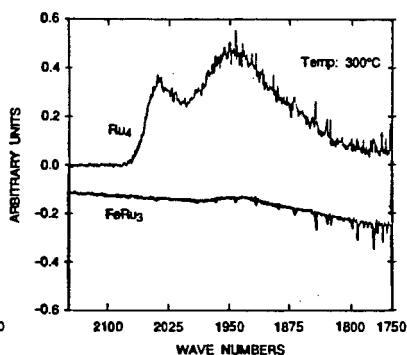[c]Not detected.
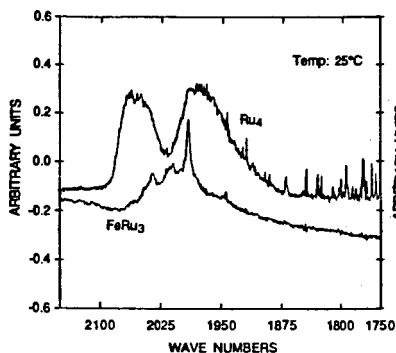
FIGURE 1: COMPARISON OF Ru$_4$ AND FeRu$_3$ CLUSTERS ON MgO UNDER N$_2$.
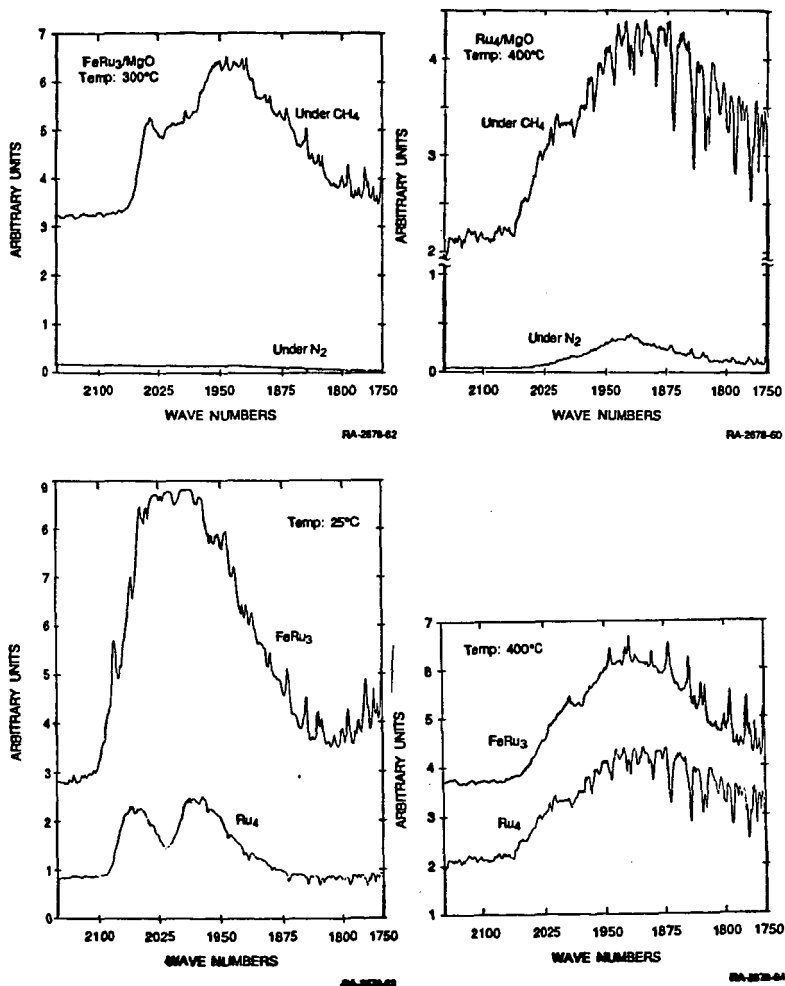
FIGURE 2: COMPARISON OF Ru$_4$ AND FeRu$_3$ CLUSTERS ON MgO UNDER CH$_4$.